

The University of Chicago

# A STUDY OF LIQUID LENSES

A PART OF A DISSERTATION SUBMITTED TO  
THE GRADUATE FACULTY IN CANDIDACY FOR  
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1931

By

JOSEPH JOHN JASPER

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## A STUDY OF LIQUID LENSES

### INTRODUCTION

The fact that some organic liquids will not spread upon water has been observed by several investigators. These non-spreading liquids were found to assume the form of lenses with various degrees of curvature and to float upon the surface of water without changing shape. In 1921, Harkins and Feldman,<sup>1</sup> during their investigation of the spreading of organic liquids on water, found that of 89 liquids used, 20 of them failed to spread. They sought an explanation of this through the thermodynamics of surfaces and arrived at the concept of the spreading coefficient. This they used as a criterion for spreading.

The most important theories regarding the criterion for spreading which have been advanced up to the present time are listed as follows:

1. All liquids spread on a pure surface.
2. A liquid a will spread on a liquid b if  $T_b > T_a + T_{ab}$ , in which  $T_a$  and  $T_b$  represent the surface tensions of the respective liquids a and b, and  $T_{ab}$  their interfacial tension. Then, if the condition  $T_b < T_a + T_{ab}$  exists, there can be no spreading.
3. Liquids whose molecules are polar, or contain polar groups, spread on water.

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<sup>1</sup>J.A.C.S. 44 (1922).

4. A liquid will spread if its work of surface cohesion is less, and will not spread if its work of surface cohesion is greater, than its work of adhesion with respect to the surface of the liquid or solid upon which the spreading takes place.<sup>1</sup>

The second criterion for spreading, as given above, was derived from a consideration of the Neumann equilibrium triangle, and it was for the purpose of testing this theory that this investigation was undertaken.

Maxwell,<sup>2</sup> in his treatment of the subject of capillarity, discusses the Neumann triangle, as follows:

If the three fluids can remain in contact with one another, the sum of any two of the quantities (interfacial tensions) must exceed the third, and by Neumann's rule the directions of the interfaces at the common edge must be parallel to the sides of a triangle, taken proportional to  $Aab$ ,  $Bbc$ ,  $Cca$  (see figure 1). If the above-mentioned condition is not satisfied, the triangle is imaginary, and the three fluids can not rest in contact; the two weaker tensions, even if acting in full concert, being incapable of balancing the strongest.

This theory, as set forth, assumes that the surface tension of the supporting liquid is acting in one direction, while the surface tension of the lens liquid, together with the interfacial tension of the two liquids, is acting in the opposite direction. Any resulting motion of the edge of the lens occurs, then, in the direction of the greater pull. This theory further demands that the angles should be controlled entirely by the surface tension forces and in such a way that at the edge of

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<sup>1</sup>J.A.C.S. 44 (1922).

<sup>2</sup>J. C. Maxwell. Capillarity, Encyc. Brit., 11th ed., vol. 5, p. 263.

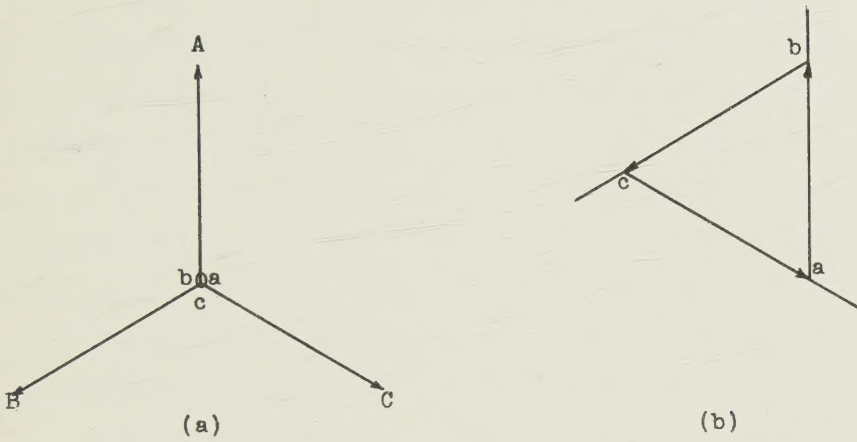


Figure 1.- The Neumann equilibrium triangle.

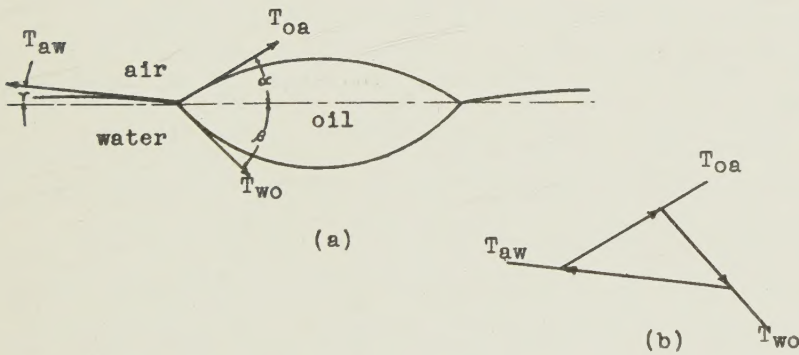


Figure 2.- Application of forces to the Neumann triangle.



the lens the three surface tensions are in statical equilibrium, i.e., their net sum is equal to zero.

Since it is an observed fact that three fluids can remain in contact with one another (a gas such as air being regarded as one of the fluids), it is evident that they must meet each other at definite angles. If the lens formed by the non-spreading liquid is stable, these contact angles must have constant values, and the interfacial forces must balance. When this condition exists, the three interfacial forces acting may be represented by vectors, and these, together with the observed contact angles, constitute the Neumann force triangle. This is shown in figure 2.

The contact angles of the lenses formed by carbon tetrachloride, carbon disulphide, cyclohexane, and a paraffin oil were studied by Hardy.<sup>1</sup> From his work he obtained evidence which agreed with the theory as outlined above, though Rayleigh,<sup>2</sup> Worthington,<sup>3</sup> Quincke,<sup>4</sup> and others do not agree with this point of view. Coghill and Anderson<sup>5</sup> calculated the values of the contact angles formed by means of the surface tensions and interfacial tensions of the following liquid pairs: Paraffin oil on water, carbon tetrachloride on water, benzene on aqueous sodium oleate solutions, and a paraffin oil

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<sup>1</sup>Hardy. Proc. Roy. Soc., A, 86, 61 (1912).

<sup>2</sup>Rayleigh. "Scientific Papers," III, 351, 397, 513, 562, 572 (1887-1892).

<sup>3</sup>Phil. Mag. (5) 18, 364 (1884).

<sup>4</sup>Quincke. Phil. Mag. 41, 454 (1871).

<sup>5</sup>Bureau of Mines Tech. Paper 262 (1924).



on aqueous acetic acid solutions. They compared the values of their observed contact angles with their calculated values, some of which agreed very closely. They attributed the cases of disagreement to the fact that the interfacial tension tests were not made under the same conditions as those under which the cathetometer readings were taken. Lyon,<sup>1</sup> in his photomicrographic study of floating lenses, found some variation between the values of the observed and the calculated angles. He accounted for this from the fact that the lenses which he studied were small and therefore the internal pressure effect, as pointed out by Worthington,<sup>2</sup> would be considerable.

#### EXPERIMENTAL

In the present investigation the contact angles of a series of non-spreading organic liquid-water pairs were measured by a photomicrographic method. The apparatus (see plates 1 and 2) consisted essentially of a camera equipped with a long bellows-draw with rack and pinion focus movement, a compound microscope having both a horizontal and vertical motion and mounted with its axis horizontal, a vertical micro-motion shelf for raising and lowering the glass cell, a glass cell, and a 500-watt mazda light source with a reflector. The cell was constructed of optically plane glass and had internal dimensions 8 by 8 by 5 centimeters. As the lenses studied

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<sup>1</sup>Lyon. J. Chem. Soc. of London, (April, 1930).

<sup>2</sup>Phil. Mag. 20, 51 (1885).

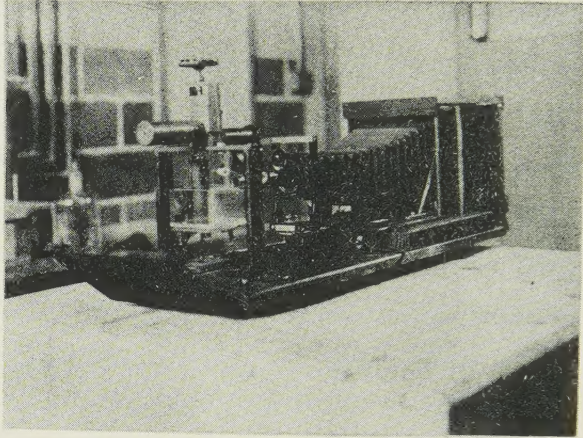


Plate 1.- Assembled photomicrographic apparatus.

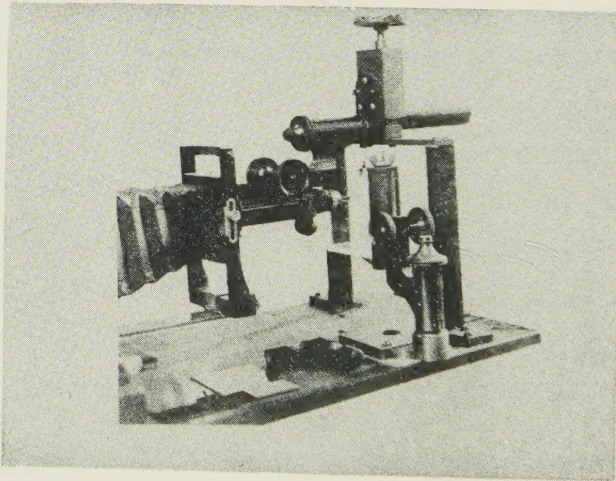


Plate 2.- The adjusting mechanism.

were moderately small, their diameters averaging 0.6 centimeters, these dimensions not only allowed of sufficient area to insure a plane water surface, but brought the central region to the proper distance from the optical system, thus making it possible to obtain a sharp focus with the objective used when the liquid lens under consideration was floating in the region of the center of the water surface.

After the apparatus was assembled and adjusted, it was tested for distortion by the three following methods:

1. A graduated scale was photographed both in a horizontal and in a vertical position. It was found that the magnification was the same in both cases.

2. Objects having known angles were suspended under the water surface in the cell and perpendicular to the direction of vision. These were photographed and the values of the angles of the image compared with the known values of these angles. They agreed in every case.

3. A circular object suspended as described above gave a circular image on the photograph.

From a consideration of the photographs described above, it was concluded that this photomicrographic method would give images of the lenses studied which would represent their true shape.

The organic liquids used were of a known high degree of purity. In the case of the two paraffin oils, petrolatum and stanolax, no information was available.



## PROCEDURE

The preliminary procedure consisted, in every case, in carefully cleaning the cell with chromic acid, followed with several rinsings with conductivity water. The cell was then placed upon the vertical motion shelf and filled to overflowing with a high grade conductivity water. The surface of the water was then adjusted until the cell was but slightly overfilled. The organic liquid was then delivered to the center of the water surface by means of a small glass rod which was ground on one end, care being taken that each drop should fall on the lens formed by the previous drops. This was done to prevent water from being drawn into the lens, since it had previously been observed that drops touching the water surface before coalescing gave a flatter lens.

The lens which was formed by the non-spreading organic liquid was held loosely in position by a bronze wire of 0.07 millimeters diameter, the end of which just touched the liquid surface. This wire was looped around a glass rod which was held suspended above the cell. This enabled it to swing freely. The glass rod around which the wire was looped, was held in position by a cork through which the rod passed. This cork in turn was suspended by another glass rod by which it was raised and lowered or swung in an arc. These combined motions made it possible to move the bronze wire in any direction desired. Since the diameter of the wire was about  $1/85$  as great as that of the lenses, it was assumed that it had no appreciable effect

on their shape or their contact angles. The water surface was illuminated with a horizontal beam of light and the floating lens viewed with the microscope, which was mounted horizontally. The image of the lens was projected upon the focal plane of a camera and a photograph of the magnified image made. The magnification was between 195 and 200 diameters.

Because of the effect of the water meniscus on the cell walls, two photographs of each lens was necessary. For the first of these, the cell was slightly overfilled so that the water surface curved downward, as shown in figure 3. From this surface the portion of the lens protruding above the water surface was photographed. A light screen was used for this portion of the lens. This served to cut off reflected rays from below the water surface, which obscured the point of contact of the liquid lens with the water. For the second photograph water was withdrawn until the cell was about three-quarters filled. In this case the water meniscus curved upward, which allowed the portion of the lens below the water surface to be photographed.

Since the liquid lenses which were investigated floated upon the water surface between the light source and the microscope objective, their projected images appear as silhouettes with sharp outlines. It was found that the light diffracted by the spherical surface of the lens, together with the halation effects produced by the plate, tended to over-expose that portion of the plate which registered the outline of the liquid lens. This resulted in a weak outline on the print,

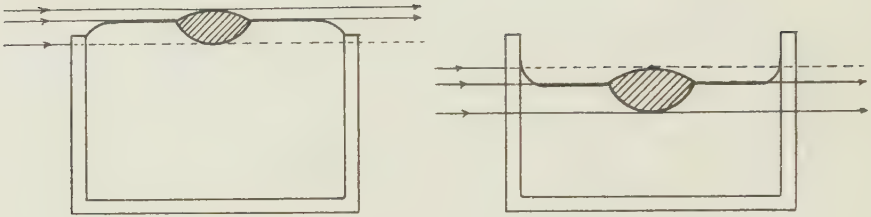


Figure 3.- The floating lenses, illustrating the methods of photographing the upper and lower portion.

which made accurate measurements of the contact angles more difficult. This effect was corrected to a considerable extent by giving a short exposure. The best exposures were found to be  $1/25$  second for the upper portion of the lens and  $1/5$  second for the lower. A strong contrast hydrochinone developer was used for development.

The method outlined thus furnished a means for photographing the common meeting point of air, water, and a non-spreading organic liquid. This common meeting point, together with the curvature of each liquid toward this point, gave the necessary material for measuring the contact angles.

Lipka,<sup>1</sup> in his discussion of graphical differentiation,

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<sup>1</sup>Lipka. Graphical and Mechanical Computation, (1918), p. 244.



suggested a method which seemed to the writer to be far superior to that of the protractor for measuring the contact angles. Since accurate use of the protractor demands that the observer recognize the point where the angle arm is just tangent to the curve at the contact point of the liquids, great difficulty is encountered, especially for small curvatures. Though this method was first tried, it was soon abandoned in favor of the method suggested by Lipka, which is about to be described.

In making the contact prints from the negatives obtained by photographing the lenses, a sheet of thin cross-sectioned paper, which was divided into millimeter squares, was placed upon the emulsion side of the negative and carefully aligned. This paper had previously been treated with a transparentizing liquid. The developing out paper was placed upon this cross-sectioned paper and then exposed. The result was a print which showed the image of the lens divided into millimeter squares. The vertical and horizontal lines which intersected the edge of the lens image offered a means for determining a series of consecutive, approximate slopes at definite distances along the curve. This was accomplished in the following manner: A low power microscope, which was equipped with cross hairs and a screw motion along a scale in one direction, was placed in such a position that the tube was movable over a shelf upon which the print was placed. This is shown in plate 3. This shelf was in turn actuated by a screw motion in a direction perpendicular to that of the microscope

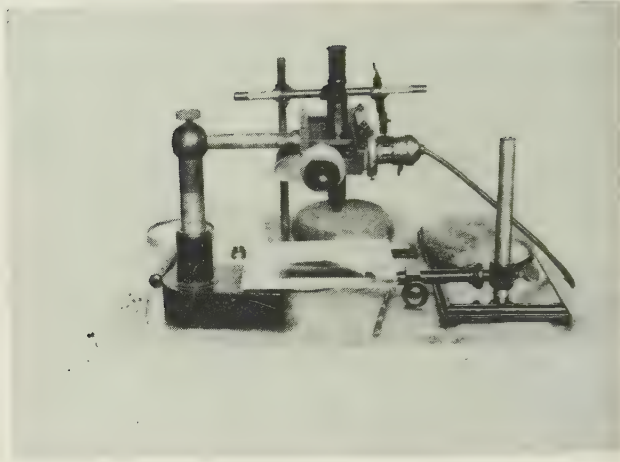


Plate 3.- Apparatus for determining derivative curves.

motion. The print was fastened upon the shelf in such a position that the vertical cross section lines were parallel to the direction of motion of the microscope. The horizontal cross section lines were then parallel to the direction of motion of the shelf. Since the distance between each perpendicular line was known, it was only necessary to measure accurately the distance between the edge of the lens image and the first horizontal line. In this manner, the average slope of the curve between each perpendicular line was determined. These average slopes were plotted as ordinates against the distance in millimeters from the point of contact of the

two liquids as abscissa.\* From this, a derivative curve was obtained. This curve, extrapolated to zero, gave the value of the tangent at the zero point, which corresponded to the contact point of the two liquids. Since this tangent was known, the corresponding angle was readily obtained.

The surface and interfacial tensions of the liquids were determined at the temperature prevailing in the laboratory when the photographs were made. The ring method, as standardized by Harkins and Jordan<sup>1</sup> in this laboratory, was used, and their corrections were applied in all calculations. For the surface tension measurements, the conditions of the experiment were approximated as closely as possible, i.e., while making the water surface tension measurements, a lens of organic liquid was allowed to float on the surface out of range of the area needed for the ring as the pull was applied. Before measuring the organic liquids, they were thoroughly wet with water by shaking the two liquids in a separatory funnel. Ring number 10 was used in all surface tension measurements. For the interfacial measurements, ring number 5 was used. The latter size was used in accordance with the recommendation made by Harkins and Jordan.

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\*It is obvious that the actual "contact point" of the two liquids is a circle. Since the outline corresponding to a vertical cross section of the two liquids is shown only, this "contact point" becomes a true point, or two points, if the whole lens is considered.

<sup>1</sup>Harkins and Jordan. J.A.C.S. 52, 1751 (1930).

## DISCUSSION

In figure 2a, page 3, are shown the angles whose values are indicated in Table II, page 26. From the figure, it is seen that angle  $\alpha$  is included between the horizontal passing through the two contact points of the liquids and the tangent of the curve of the upper portion of the lens liquid at the contact point. Angle  $\beta$  is formed by the intersection of the horizontal and the tangent to the curve of the lower portion of the lens liquid at the contact point of the two liquids. Angle  $\gamma$  is then formed by the intersection of the horizontal and the tangent to the curve formed by the supporting liquid at the contact point of the liquids. In figure 2a these tangents are indicated by vectors, the magnitude of which represent the value of the tensions of the liquids, and the directions of which indicate the direction of pull of their horizontal components. These vectors make up the sides of the Neumann force triangle.

Of the three angles measured, the one most difficult to obtain was  $\gamma$ . Measurements for this angle were made from both the upper and lower photographs of the lenses. When the values of this angle, as obtained from the two photographs, were compared, it was found that the value obtained from the upper photograph was somewhat greater than that obtained from the lower in every case. Since this angle, as viewed in the photograph of the upper portion, has passed horizontally through a meniscus of a liquid lens, as shown in figure 4,



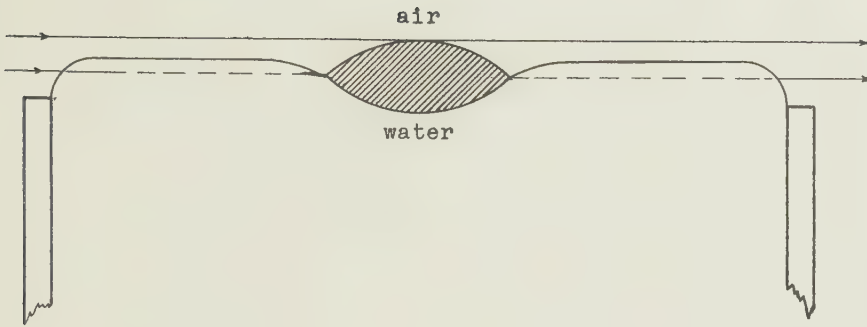


Figure 4.- The meniscus effect of the supporting liquid.

there is some possibility of distortion. For the same reason the value of the  $\alpha$  angle may not be exactly correct. Since the possibility of distortion was not evident in the lower photograph, the values of  $\gamma$  as determined from this side of the water surface were chosen.

The simple theory as set forth by Maxwell<sup>1</sup> demands that the angles should be entirely controlled by surface tension forces in such a way that the three surface forces are in statical equilibrium. This requirement may be expressed by the two following equations:

$$\sigma_{ao} \cos \alpha + \sigma_{ow} \cos \beta - \sigma_{aw} \cos \gamma = 0 \quad (1)$$

$$\sigma_{ao} \sin \alpha + \sigma_{aw} \sin \gamma - \sigma_{ow} \sin \beta = 0 \quad (2)$$

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<sup>1</sup>J. C. Maxwell. Capillarity, Encyc. Brit., 11th ed., vol. 5, p. 263.

In these equations  $\sigma_{Oa}$  indicates the surface tension air-organic liquid,  $\sigma_{Ow}$  the interfacial tension organic liquid-water, and  $\sigma_{aw}$  the surface tension air-water.

From consideration of figure 2a, page 3, and the above equations, it is evident that if equilibrium is to exist between any liquid pairs, any change which results in a change of the components of the balanced forces must result in a rearrangement of the components in such a manner that the forces again arrive at equilibrium. It is clearly evident by consideration of figure 2a, that if  $T_{aw}$  is increased, thereby increasing its horizontal component, either  $T_{ao}$ , or  $T_{ow}$ , or both, must increase if the lens does not spread. By increasing these tensions, both their horizontal and vertical components are increased, and the contact angles remain constant.

If the values of the angles remain constant, it is evident that the shape of the lens must remain constant and in the same position with respect to the plane of the water surface. It is likewise evident that if a solute were added to the supporting liquid, which had but little effect on the surface tensions of the two liquids but decreased their interfacial tension, the horizontal component of this tension would immediately decrease. To balance this effect, the horizontal component of the surface tension of the lens would have to increase. This could only take place through a decrease in the value of angle  $\alpha$ . This angle can decrease only by a decrease in the height of the portion of the lens above the water. It is obvious that this can be done by either of two

ways, namely, the lens can spread, or it can sink deeper into the supporting liquid. Since the surface tension of the lens liquid does not decrease, the lens can not spread.\* It must, then, sink farther into the supporting liquid and the area of the interface increase at the expense of the upper surface. Lyon,<sup>1</sup> in his study of hydrochloric acid solution-oleic acid pairs, in which the concentration of the hydrochloric acid solution was varied, was able to change the  $\theta$  angle from 20 to 157 degrees, thus almost totally submerging the lens.

The value of the  $\tau$  angle is due entirely to the depth to which the floating lens sinks into the supporting liquid. This depth is in turn controlled by a combination of forces which act in the same direction, namely, the buoyancy of the supporting liquid and the vertical component of its surface tension. The resultant of the total vertical forces acting upon the floating lens is zero. This can be shown by use of the following equation, in which it is assumed that the lens is made up of two spherical segments:

Let  $F_1$  = total value of the vertical component of the  
surface tension of the supporting liquid

$F_2$  = supporting force due to buoyancy of the  
supporting liquid

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\*A liquid can spread on water only if its spreading coefficient is positive, i.e., if the work of adhesion is greater than the work of cohesion. For a lens floating on water, and thus having a negative spreading coefficient, spreading would necessitate the decrease in surface tension of the lens liquid, since surface tension is a direct measure of its cohesive work. Such a decrease would change the coefficient in a positive direction, and the tendency to spread would increase.

<sup>1</sup>Lyon. J. Chem. Soc. of London. (April, 1930).

$F_3$  = force tending to cause the lens to sink  
into the supporting liquid

It is evident, then, that

$$F_1 = F_3 - F_2$$

and since

$$F_1 = 2\pi r \sigma_{aw} \sin \gamma$$

and

$$F_2 = 1/3\pi D_2 h_2^2 (3r - h_2)g$$

and

$$F_3 = 1/3\pi D_1 [3r(h_1^2 + h_2^2) - (h_1^3 + h_2^3)]g$$

these can be substituted in the force equation above. We then obtain the following equation:

$$2\pi r \sigma_{aw} \sin \gamma = 1/3\pi g \left\{ D_1 [3r (h_1^2 + h_2^2) - (h_1^3 + h_2^3)] - D_2 h_2^2 (3r - h_2) \right\} \quad (3)$$

in which

$D_1$  = density of the lens liquid

$D_2$  = density of supporting liquid

$h_1$  = height of spherical segment composing  
the upper portion of the lens

$h_2$  = height of spherical segment composing  
the lower portion of lens

$r$  = radius of lens

$g$  = gravity

In order to test this equation,  $D_1$  and  $D_2$  must be known at the temperature of the experiment. Knowing the magnification of the image, we can readily obtain  $h_1$ ,  $h_2$ , and  $r$  from measure-



ments of the photograph. Table I gives the results of the measurements of the lenses of fifteen of the liquids used.\* The values of  $h_1$ ,  $h_2$ , and  $r$  are given in centimeters.

The results of the study of the organic liquid lenses are tabulated in Table II, page 26. It is evident that the various factors, surface tensions, interfacial tensions, and contact angles, which are dealt with in equations 1 and 2, are influenced in some manner by the temperature. Since it was not possible to regulate the temperature of the laboratory, it became necessary to determine a complete set of data for each lens at the temperature prevailing in the laboratory when the photographs were made. These temperatures, in degrees centigrade, are tabulated in column 1. By substituting the proper values in equation 1, the value of the resultant force is obtained. These forces are tabulated in the last column of Table II. It is evident that the resultant force should equal zero in each case if the simple theory of the Neumann equilibrium triangle is valid. Since this is not the case, it becomes evident at once that equations 1 and 2 must be modified. Lyon<sup>1</sup> has made an attempt to do this, using the principle of virtual work, though his calculated and observed values seriously disagree for water lenses on organic liquids.

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\*These fifteen liquids were chosen from the group due to the fact that, according to the writer's notes, they are the only ones whose magnifications were known for certain, i.e., they were floating in exactly the same position as that of the scale when it was photographed. Consequently their dimensions can be determined by measurement of the photographs.

<sup>1</sup>Lyon. J. Chem. Soc. of London, (April, 1930).

TABLE I

THE EQUILIBRIUM FORCES AND LENS DIMENSIONS OF FIFTEEN  
NON-SPREADING LIQUIDS ON WATER

| Organic Liquids             | $h_1$  | $h_2$  | $r$   | $D_1$ | $D_2$ | $F_1$ | $F_3 - F_2$ | $\Sigma F$ |
|-----------------------------|--------|--------|-------|-------|-------|-------|-------------|------------|
| Acetylene tetrabromide      | 0.027  | 0.106  | 0.197 | 2.949 | 0.996 | 11.78 | 11.90       | -0.12      |
| Methylene iodide            | 0.0025 | 0.115  | 0.166 | 3.308 | 0.996 | 12.28 | 12.31       | -0.03      |
| Carbon disulphide           | 0.0246 | 0.0352 | 0.324 | 1.425 | 0.996 | 1.26  | 1.30        | -0.04      |
| $\alpha$ -bromo naphthalene | 0.060  | 0.092  | 0.257 | 1.475 | 0.996 | 7.02  | 7.07        | -0.05      |
| Nitrobenzene                | 0.040  | 0.080  | 0.415 | 1.197 | 0.996 | 4.40  | 4.10        | +0.30      |
| Bromoforn                   | 0.016  | 0.050  | 0.253 | 2.914 | 0.996 | 4.87  | 4.20        | +0.67      |
| P-bromo-toluene             | 0.028  | 0.031  | 0.300 | 1.380 | 0.996 | 0.59  | 0.71        | -0.12      |
| O-bromo-toluene             | 0.014  | 0.014  | 0.387 | 1.411 | 0.996 | 0.00  | 0.46        | -0.46      |
| Diphenyl dichloro methane   | 0.042  | 0.091  | 0.352 | 1.165 | 0.996 | 4.10  | 3.50        | +0.60      |
| Cyclo hexane                | 0.044  | 0.036  | 0.280 | 0.773 | 0.996 | 1.22  | 0.51        | +0.67      |
| $\alpha$ -chloronaphthalene | 0.056  | 0.064  | 0.253 | 1.177 | 0.996 | 3.90  | 3.28        | +0.52      |
| Tribromo hydrin             | 0.019  | 0.111  | 0.260 | 2.439 | 0.996 | 11.46 | 12.31       | -0.85      |
| Phenyl mustard oil          | 0.042  | 0.063  | 0.246 | 1.119 | 0.996 | 1.89  | 1.74        | +0.15      |
| Iodo benzene                | 0.040  | 0.100  | 0.280 | 1.819 | 0.996 | 9.85  | 9.34        | +0.51      |
| Carbon tetrachloride        | 0.007  | 0.013  | 0.264 | 1.577 | 0.996 | 0.00  | 0.07        | -0.07      |

$h_1$  = height of spherical segment composing the upper portion of the lens

$F_1$  = total value of the vertical component of the surface tension of the supporting liquid

$h_2$  = height of spherical segment composing the lower portion of lens

$F_2$  = supporting force due to buoyancy of the supporting liquid

$r$  = radius of lens

$D_1$  = density of the lens liquid

$D_2$  = density of supporting liquid

$F_3$  = force tending to cause the lens to sink into the supporting liquid

Coghill and Anderson,<sup>1</sup> while studying lenses of carbon tetrachloride on water, observed that the floating liquid formed a flattened globule and as such would not permit the assumption that each lens portion was made up of spherical segments. By careful observation of the photographs of the lenses studied in this investigation, it was found that practically none of these lenses were made up of true spherical segments, even when the lens liquid consisted of water. In the latter case, it was observed that the surface of the supporting organic liquid inclined upward to meet that of the water, i.e., the vertical component of the surface tension of the supporting liquid was directed downward. If the density of the water lens is equal to or greater than that of the supporting organic liquid, the lens would be drawn below the organic liquid surface, especially if the organic liquid spreads upon the water. For the above reasons it would not be expected that equation 3 would hold closely in all cases. Because of its relatively high surface tension, it would not be expected that water would spread on any organic liquid. By application of equation 1, then, it is seen that the sum of the forces tending to prevent the spreading is so great that the water lens would almost assume the shape of a perfect sphere. Studies of water lenses on carbon tetrachloride, carbon disulphide, stanolax, monobromobenzene, and even benzene, the photographs of which are not included in this report, show this to be true. The

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<sup>1</sup>Bureau of Mines Technical Paper 262. (1924).

lens which rested on benzene was very small but almost perfectly spherical.

Since oleic acid and mononitrobenzene have a positive spreading coefficient on water, it is evident that any lenses formed by these liquids would consist of the excess liquid after spreading had taken place. This was found to be true from the decrease in the surface tension of the supporting liquid. Diphenyl methane and diphenyl ethane, though appearing to spread, were found to form minute lenses, which upon standing coalesced to some extent. Photographs were made of lenses of these two liquids on water, but due to the fact that their densities are practically the same as that of water, it was found impossible to measure their interfacial tensions with water by means of the ring method. For this reason they were omitted from Table II.

It was observed by the writer that in several cases where the lenses were allowed to float on the water surface for several hours, some spreading had taken place. A lens of stanolax, for example, after eight hours was found to cover an area about twice as large as it had formerly. This could occur only by (1) an increase in the horizontal component of the surface tension of the water, (2) a decrease in the horizontal component of the surface tension of the lens liquid, (3) a decrease in the horizontal component of the interfacial tension, or (4) a combination of the above. Any change in these horizontal components would depend upon a change in their respective tensions. Since solution of the lens liquid would



decrease the surface tension of the water somewhat, such a process would not explain the relatively increased pull exerted by the horizontal force of the water unless accompanied by a much greater decrease in the forces pulling in the opposite direction. The latter might be brought about by the wetting of the lens liquid, which would tend to decrease the surface tension of the organic liquid. Simultaneously with this, there was probably a decrease in the interfacial tension. In the photographic procedure, no time was lost between the introduction of the organic liquid to the surface of the water and the photographing of the resulting lens, so it seems safe to assume that the angles obtained in all except the cases of mononitrobenzene and oleic acid are the true contact angles existing between the two liquids, neither of which has been appreciably modified.

The fact that the net sum of the horizontal forces acting upon the lens does not equal zero, as shown by the last column of Table II, leads to the supposition that some forces are being overlooked in the attempt to test the validity of the Neumann equilibrium equation. Lyon, in his studies, used lenses whose diameters were much smaller than those used in this investigation. Coghill and Anderson used lenses considerably larger and their results in many cases are much better. It was evident early in this investigation that a large lens was preferable to a small one, but due to the fact that in practically all cases the density of the lens liquid was greater than that of water, it was found impossible to obtain

a very large lens which would not sink. By referring to Table II, page 26, it will be found that some of the organic liquids used had densities as much as three times that of water. Preliminary experiments showed that as the size of the lens increased, the shape approached more and more that of a flattened globule. In such a lens the existing curvature along the upper portion decreased until it was almost zero, while the curvature in the vicinity of the contact point of the two liquids appeared to remain constant. It would seem, then, that in a large lens other forces, such as internal pressures caused by curvature of the lens, would become negligible in comparison to surface tension forces which were acting. Such lenses would be very difficult to obtain for the reason stated above, unless liquids having a smaller density than water were used. Coghill and Anderson found that the angles best agreeing with the theoretical values of the equilibrium triangle were obtained from lenses having diameters of about four centimeters.

By referring to the column of contact angles in Table II, it will be seen that three of the  $\gamma$  angles are assigned zero values. In these cases this angle was very small and consequently difficult to measure with any degree of accuracy. Though it is probable that the true values of these  $\gamma$  angles are greater than zero, it appears equally certain that they are not greater than fifteen minutes. Consequently the difference between the measured surface tension of the supporting liquid and its horizontal component is negligible.

It is a well-known fact that many of the compounds used in this investigation undergo hydrolysis. That this may have occurred to some extent is undoubtedly true. Since the horizontal components of the tensions would be affected by hydrolysis, such a reaction could account for the deviations of the summation of the forces from zero (listed in the last column of Table II) only if these tensions were considerably changed. Since the deviation is in the negative direction in all cases but one, this would indicate that either (1) the surface tension of the water had been increased, (2) the interfacial tension of the liquid pairs decreased, (3) the surface tension of the organic liquid decreased, or (4) a combination of these effects took place. Surface tension measurements of each liquid pair in the presence of each other showed a difference from that of the pure liquids only in the cases of mononitrobenzene and oleic acid. In these cases the surface tension of the water was decreased due to the initial spreading of the organic liquid upon the water surface.

It becomes evident, then, that any effect of hydrolysis was to decrease the interfacial tension. From Table II it is seen that such compounds as stanolax, petrolatum, and cyclohexane, which do not hydrolyze at all, give the greatest negative deviation, while the others vary irregularly. It was concluded, therefore, that the effect of hydrolysis was negligible.

TABLE II  
SURFACE TENSIONS, INTERFACIAL TENSIONS, AND  
CONTACT ANGLES OF THE LIQUID PAIRS

| Organic liquid                       | Temperature during experiment in °C. | Density of wet lens liquid at the given temperature | Surface tension of lens liquid | Surface tension of supporting liquid | Interfacial tension | Contact angles |         |          | $\Sigma \sigma \cos \theta$ |
|--------------------------------------|--------------------------------------|-----------------------------------------------------|--------------------------------|--------------------------------------|---------------------|----------------|---------|----------|-----------------------------|
|                                      |                                      |                                                     |                                |                                      |                     | $\alpha$       | $\beta$ | $\gamma$ |                             |
| $\alpha$ -bromonaphthalene           | 28.0                                 | 1.475                                               | 43.7                           | 71.5                                 | 41.3                | 16°30'         | 27°30'  | 3°30'    | -7.1                        |
| Monobromobenzene                     | 33.2                                 | 1.477                                               | 35.5                           | 70.7                                 | 38.8                | 4°0'           | 8°0'    | 10°30'   | -3.1                        |
| Mononitrobenzene                     | 31.2                                 | 1.197                                               | 42.0                           | 64.6                                 | 24.9                | 9°40'          | 19°40'  | 10°30'   | -0.8                        |
| Methylene iodide                     | 28.3                                 | 3.308                                               | 49.4                           | 71.4                                 | 44.9                | 14°20'         | 55°30'  | 9°30'    | -3.1                        |
| Iodobenzene                          | 27.7                                 | 1.819                                               | 38.7                           | 71.5                                 | 41.1                | 17°20'         | 29°00'  | 4°20'    | -1.0                        |
| Bromoform                            | 28.7                                 | 2.914                                               | 40.5                           | 71.3                                 | 39.9                | 4°0'           | 15°30'  | 2°30'    | -7.5                        |
| Tri bromohydrin                      | 28.8                                 | 2.439                                               | 44.2                           | 71.3                                 | 37.9                | 9°40'          | 35°00'  | 5°40'    | -4.6                        |
| Tri bromoethylene                    | 28.6                                 | 2.668                                               | 40.8                           | 71.3                                 | 37.2                | 1°30'          | 20°30'  | 6°40'    | -4.6                        |
| Para-bromotoluene                    | 31.8                                 | 1.880                                               | 35.5                           | 70.9                                 | 38.5                | 18°30'         | 8°00'   | 1°40'    | -0.4                        |
| Ortho-bromotoluene                   | 28.8                                 | 1.411                                               | 34.6                           | 71.3                                 | 40.8                | 5°50'          | 3°20'   | 1°0'     | -3.8                        |
| $\alpha$ -chloronaphthalene          | 32.9                                 | 1.177                                               | 40.2                           | 70.8                                 | 39.7                | 20°30'         | 25°20'  | 2°0'     | -2.9                        |
| Ethylene dibromide                   | 33.0                                 | 2.154                                               | 37.5                           | 70.7                                 | 35.6                | 5°0'           | 21°50'  | 9°0'     | -0.5                        |
| Carbon disulphide                    | 30.7                                 | 1.245                                               | 32.8                           | 71.1                                 | 47.7                | 9°0'           | 6°40'   | 0°30'    | -8.5                        |
| Carbon tetrachloride                 | 28.9                                 | 1.577                                               | 26.5                           | 71.2                                 | 44.2                | 2°50'          | 3°50'   | 0°30'    | +0.6                        |
| Tetrachlorethylene                   | 27.8                                 | 1.616                                               | 30.8                           | 71.5                                 | 47.0                | 5°20'          | 6°00'   | 2°30'    | -5.9                        |
| Acetylene tetrabromide               | 28.8                                 | 2.949                                               | 47.9                           | 71.3                                 | 38.1                | 13°20'         | 39°40'  | 7°30'    | -5.3                        |
| Phenyl mustard oil                   | 33.4                                 | 1.119                                               | 39.6                           | 70.6                                 | 38.0                | 15°40'         | 26°00'  | 1°0'     | -1.7                        |
| Oleic acid                           | 32.7                                 | 0.885                                               | 32.1                           | 42.6                                 | 14.8                | 3°0'           | 12°00'  | 0°00'    | -3.8                        |
| Stanolax                             | 25.6                                 | 0.940                                               | 30.5                           | 71.8                                 | 55.5*               | 9°20'          | 11°30'  | 1°30'    | -13.8                       |
| Petrolatum                           | 29.8                                 | 0.870                                               | 30.9                           | 71.2                                 | 55.3*               | 9°50'          | 6°00'   | 2°50'    | -14.6                       |
| Cyclo hexane                         | 26.6                                 | 0.773                                               | 24.4                           | 71.6                                 | 60.1                | 14°40'         | 10°00'  | 0°00'    | -11.1                       |
| Diphenyl dichloro methane            | 29.7                                 | 1.165                                               | 42.6                           | 71.2                                 | 39.4                | 15°40'         | 27°00'  | 1°30'    | -5.4                        |
| Water on nitrobenzene                | 31.2                                 | 0.996                                               | 64.6                           | 42.0                                 | 24.9                | 2°00'          | 120°30' | 0°00'    | -2.2                        |
| Water on $\alpha$ -chloronaphthalene | 32.9                                 | 0.996                                               | 70.8                           | 40.2                                 | 39.7                | 28°40'         | 119°00' | 5°20'    | -4.0                        |

\*These values were determined by Harkins and Feldman.



## SUMMARY AND CONCLUSIONS

1. A photomicrographic method was used to obtain in silhouette the shape and curvature, at the common meeting point, of twenty-four liquid pairs. One member of each pair was floating upon the other in the form of a liquid lens.

2. The apparatus used was designed and assembled in this laboratory and has been described in detail. Preliminary photographic tests for distortion were carried out under the same conditions as the experiments. These photographs showed no distortion.

3. The tangents to the curves at the common meeting point of the liquid pairs were determined by the derivative curve method, which has been described. From these tangents the contact angles were obtained. It was found that these angles vary widely with the liquid pairs used.

4. The surface tensions of the liquids and the interfacial tensions of the liquid pairs were determined by the ring method as standardized by Harkins and Jordan.

5. The theory underlying the Neumann equilibrium triangle was discussed and the necessary data applied in the Neumann equation. From the results obtained it was found that the net sum of the forces did not equal zero for any of the liquid pairs studied, though deviation of several are well within the limits of experimental error. The three paraffins, stanolax, petrolatum, and cyclo hexane, show the greatest

deviation. It was finally concluded that the equation should be modified in some way for small lenses.

6. For large lenses it is probable that the Neumann equation would hold, since all forces other than the surface tensions would become negligible.

7. Since the observed force summations vary irregularly between liquids which are readily hydrolyzed and those which do not hydrolyze, it was concluded that the effect of hydrolysis upon the equilibrium factors was negligible.









